



TRANSLATION OF FR 2,668,951 FROM FRENCH

(54) Process for activation of hydrocracking catalysts.

(57) The invention relates to a process for activation of a hydrocracking catalyst, wherein the catalyst is activated by sulfur and by nitrogen in the hydrocracking zone in the presence of a light petroleum fraction containing sulfur and nitrogen, and possibly also in the presence of additional sulfurized and nitrogenated compounds, with the sulfur and nitrogen content of the petroleum fraction and of the additional components being higher or lower depending on whether the catalyst is meant to be presulfurized in the hydrocracking zone (in situ) or presulfurized outside of the hydrocracking zone (ex situ).

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This invention relates to a process for activation of hydrocracking catalysts in units for hydrocracking petroleum cuts. This activation is carried out in the liquid phase by injecting onto the catalyst a light petroleum cut of the kerosene or gas oil type, before treating the nominal feed of the unit, in order to ensure best sulfurization of oxides present in the catalyst and best monitoring of the activity of acid sites present on the fresh catalyst.

Hydrocracking is a catalytic process for cracking hydrocarbons in the presence of hydrogen. It allows conversion of medium or heavy distillates and possibly also deasphalted residues (atmospheric or in vacuum) in gas, jet fuel or gas oil according to the geographic and seasonal needs of markets. It can also be used to obtain light hydrocarbons (propane, butane) or bases for motor oils with improved viscometric qualities. The hydrocracking, like catalytic cracking, makes it possible to convert heavy cuts into lighter and more valuable products, but under very different conditions. The hydrocracking operates at relatively low temperatures (350 to 430°C) and under high partial hydrogen pressure (50 to 150 bars). Depending on the nature of the feed to be processed, the desired products and performances of catalysts, several process schemes have been designed. Whatever the type of process, there are always two different sections:

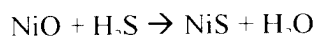
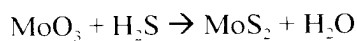
- a high-pressure section comprising one or more ovens intended to heat the feed and the hydrogen, one or more reactors, a condenser, a gas-liquid separator, a recycle gas compressor;
- a low-pressure section which stabilizes and fractionates reaction products.

The process schemes can be divided into two categories: the process scheme called "single-stage" or "series flow" and the process scheme called "two-stage" or "interstage separation". In the "series flow" process, the feed is almost always prehydrotreated on a hydrotreating catalyst to produce hydrodesulfurization, hydrodenitrogenation and hydrogenation reactions of aromatics (hydrotreating of the feed), and also possibly hydrocracking. Then the effluent from the first stage, including the gases, is transferred onto a second catalyst, a much more acid one, which carries out conversion reactions (hydrocracking). The second scheme has two stages, and an intermediate stage is also carried out in which H_2S and NH_3 are separated before the second stage, which makes it possible to "protect" the hydrocracking catalyst from high partial pressures of H_2S and NH_3 . The advantages of either of the schemes depend mainly on the required flexibility and characteristics of the feed.

A hydrocracking unit often uses several types of catalyst. As a general rule, the top catalysts are optimized to perform hydrotreating reactions. For this reason, they contain a combination of metals of the groups VI B (Mo and W) and VIII (Ni and Co), and preferably the pairs Ni Mo and Ni W. These metals are deposited in the state of oxides on a base which is often an aluminum or a mixed silica-aluminum oxide, or possibly other mixed oxides containing mainly titanium, boron, magnesium, zirconium. These catalysts may also contain phosphorus or at least a halogenate such as fluorine. These catalysts are marketed and charged into reactors while the metals are in the form of oxides; the active phase is a mixed sulfide of metals from groups VI B and VIII with a highly unique structure. The procedure for unit start-up therefore has a presulfurization phase which has to be carried out very carefully.

While the catalytic beds in the first stage perform primarily hydrotreating reactions, the catalytic beds in the second stage perform most of the hydrocracking of the feed. For this reason, catalysts which have a stronger acid function than those in the first stage are generally used. This acidity is contributed by an amorphous or crystallized aluminum silica or possibly by use of halogenated doping agents such as fluorine. The zeolites, which are crystallized aluminum silicas characterized by high acidity, are also widely used in the industry. These catalysts also have a hydrogenating function which could be contributed by a noble metal of the Palladium or Platinum type, or as above by a mixture of oxides of metals from groups VI and VIII. In this latter case, the activation procedure should also include a careful phase of sulfurizing these oxide phases.

This sulfurization stage is an integral part of the general start-up procedure of the unit. Presulfurization can be carried out using different operating methods. The corresponding chemical reactions can be written as follows, for the case of a catalyst containing nickel and molybdenum:



The sulfurizing agent can be hydrogen sulfide H_2S or another sulfurized compound, such as for example carbon sulfide, dimethyl sulfide, dimethyl disulfide, mercaptans, etc...

These sulfurization procedures can be divided into two different classes: the ones which perform this sulfurization reaction in the gas phase or the ones which use a liquid phase. Both types of methods are used in the industry.

The liquid phase is the object of patent application no. EP-B-64429, which shows that a presulfurization using a gas oil type cut with a sulfur compound as an additive, such as for example dimethyl disulfide, yields catalysts which are more active than those obtained after presulfurization in the gas phase with a mixture of hydrogen sulfide/hydrogen. The process described in the aforementioned patent is characterized in particular by the fact that the gas oil cut has no unsaturated olefin or diolefin compounds, that the sulfurized compound is injected at a relatively low temperature (less than 180°C) and that the temperature is then progressively increased using a stage-by-stage procedure until a top temperature of 300°C is reached. In this procedure, the contribution of sulfur is done from the outside by using a sulfurized precursor added in mixture to the feed.

Another means of adding the sulfur is described in EURECAT patent US-A-4.719,195. In this method, the sulfur is incorporated directly with the fresh catalyst by means of an appropriate sulfurized precursor such as an organic polysulfide. The sulfurization procedure per se, which allows conversion of the metallic oxides into sulfides, is performed in the unit without the need for exogenous contribution of sulfur, either in the gas phase under hydrogen or a gas with a high content of hydrogen, or in the liquid phase in the presence of a light petroleum cut and a gas with a high content of hydrogen.

Procedures in the liquid phase as described above cannot be applied with hydrocracking units. In fact, the liquid phase sulfurization procedure requires that a light petroleum cut (kerosene or preferably gas oil) be brought into contact with a temperature of at least 300°C or even 330 to 350°C. This heat level is necessary to ensure good conversion of the oxides into sulfides. Hydrocracking units contain at least one type of catalyst having a strong acid function, contributed for example by a zeolite. Under these conditions, this catalyst runs the risk of causing cracking of the hydrocarbon cut once temperatures hit 250 to 300°C. This uncontrolled reaction may lead to serious drawbacks; on the one hand, the catalyst risks being damaged, and prematurely deactivated

due to coking, because it will continue to work even though its hydrogenating function is not working, because it was not completely sulfurized; on the other hand, at the process level, the phenomenon is dangerous because the exothermic cracking reaction may auto-accelerate and result in 'thermal excursions' (a phenomenon called "runaway") which will damage the catalyst, then the reactors and could also cause the unit to explode.

This invention describes a means whereby this liquid-phase procedure can still be carried out, and which is preferable to the dry phase in terms of quality of sulfurization, while avoiding the untimely cracking reaction due to the catalyst's acid sites. The procedure allows control of the activity of the hydrocracking catalyst and includes a stage of passivation of the acid sites. This stage can be carried out in two different ways:

- 1) In the first method, the sulfur and nitrogen needed for the catalysts are added "in situ" in the area where hydrocracking will be carried out. A compound containing nitrogen is injected with the petroleum cut in such a way as to ensure passivation of the acid sites by means of this nitrogenated compound, just as the sulfurized compound also injected with this petroleum cut ensures sulfurization of the oxides.
- 2) In the second method, the sulfur and nitrogen needed for sulfurization and passivation are deposited on the fresh catalyst before it is charged into the hydrocracking reactor, thus "ex situ". The liquid-phase activation procedure to be performed in the hydrocracking reactor will then enable complete sulfurization of the oxides without the untimely reaction caused by the acid sites, via ex-situ pre-passivation by the nitrogenated compound.

The first method is described in more detail below. After the reactor(s) of the hydrocracking unit has or have been charged with a catalyst or different types of catalysts, at least one of which is a hydrocracking catalyst, the unit is purged by nitrogen, then by hydrogen and then pressurized until nominal pressure of the unit or possibly an intermediate pressure is reached, which is between 0.3 and 30 Mpa (Mega Pascal) and more generally between 1 and 20 Mpa. A quick depressurization test may be performed at this stage. The catalytic beds are then heated under hydrogen to a temperature below 250°C and preferably below 180°C. The liquid feed is then injected. The preferred temperature range for the injection is from 120 to 180°C. The liquid feed, which is

different from the unit's nominal feed, is mainly composed of a petroleum cut of the kerosene (or jet fuel) type or preferably gas oil (or diesel), which comes from the atmospheric distillation column. The cuts which come from conversion of heavier cuts, such as gas oils from viscoreduction or catalytic cracking processes, should be avoided. This cut preferably in fact shall have no diolefins or olefins and consequently will have a bromine index less than 5, preferably less than 2, the bromine index being measured according to the ASTM reference standard D 1159, and a nitrogen content less than 0.15%, preferably less than 0.2% by weight. This feed, intended to carry out sulfurization of the catalysts (here, therefore, "in situ" sulfurization), has a sulfur content between 0.1 and 5% by weight and preferably between 0.3 and 3% by weight, this sulfur naturally being contained in the petroleum cut, or preferably contributed in part by various sulfurized compounds such as those soluble in petroleum cuts. Thus, carbon sulfide, sulfides such as dimethyl sulfide, disulfides such as dimethyl disulfide, thiophenic compounds, mercaptans, organic polysulfides or compounds containing sulfur associated with other functions such as alcohol functions, or any other sulfurized compound capable of converting into hydrogen sulfide under these temperature and hydrogen pressure conditions and in the presence of a hydrogen sulfide catalyst. Colloidal sulfur in stable suspension in a petroleum cut can also be used.

In addition, a nitrogenated compound must be injected, at a temperature below 270°C and preferably less than 230°C. This nitrogenated compound is chosen from among the group of compounds soluble in hydrocarbons. Among these are primary, secondary, tertiary amines, compounds containing a quaternary ammonium, aryl amines such as aniline family compounds, pyrroles and their homologues, pyridines, nitriles, ureas and thioureas, nitrogenated, nitrous or nitrose derivatives, or any other basic compound or one capable of being converted into a basic compound, in particular ammoniac, under hydrogen pressure, hot and in the presence of a catalyst. This compound could also be injected in the form of gas into the hydrogen circuit. This gas could be ammoniac, for example.

The injection of sulfur and nitrogen can be monitored by measurements at the output of the reactor. Thus the sulfurized hydrogen content can be measured in the unit's recycle gas and it can be monitored to make sure it is over 0.1% by volume before bringing the temperature of the catalytic beds over 200°C and greater than 0.5% before bringing the temperature over 270°C. In fact, too

low a content of hydrogen sulfide at high temperature could promote the reduction reaction of the catalyst's oxides to the detriment of their sulfurization, which is known to be harmful to catalytic activity. Thus the ammoniac content can be measured in the wash water of the effluent, at the output of the reactor, to make sure that this content is greater than 0.2% by weight and preferably greater than 0.5% by weight before bringing the temperature of the hydrocracking catalyst up over 230°C. In fact, at a temperature below 230°C, there is no risk of a gas oil type cut cracking on a hydrocracking catalyst. Above this temperature, it must be ensured that the catalytic beds have actually been crossed by the nitrogenated compound and that the catalyst is therefore passivated.

The liquid feed flow rate, expressed in cubic meters of feed per cubic meter of catalyst and per hour, can be between 0.1 and 10, preferably between 0.2 and 5. The flow rate of hydrogen - or gas with a high hydrogen content - expressed in cubic meters of TPN [terephthalonitrile] gaseous hydrogen per cubic meter of liquid feed is between 50 and 2000 and preferably between 200 and 1500.

The activation procedure is then continued, progressively increasing the temperature at a rate of 1 to 100°C/hour and preferably of 5 to 50°C/hour, either directly to the final temperature stage, or via intermediate stages, using the methods described in French patent no. EP.B.64429. The temperature of the final stage is between 280 and 400°C and preferably between 310 and 370°C, and the time is several hours.

The activation procedure is then terminated and the unit's nominal feed can start being injected, a distillate under vacuum for example, replacing the petroleum cut used for the activation.

The second liquid-phase activation method of a unit containing at least one hydrocracking catalyst is original in the sense that the sulfur and nitrogen needed to sulfurize the oxides and to passivate the acid sites are added onto the catalyst after being produced but before charging into the reactor, thus "ex situ". Advantageously, the sulfurized and nitrogenated products described above shall be used.

The object of this invention is therefore liquid-phase activation of catalysts already containing sulfur and nitrogen before charging the feed to be treated in the unit. The procedure is described below.

The hydrocracking unit can have two major types of catalyst. Those which have a weak acid function, such as catalysts called hydrotreating catalysts, comprised for example of nickel or cobalt, molybdenum or tungsten, aluminum and possibly other elements such as phosphorus, fluorine, silicon, boron, must contain from 1 to 20% by weight of sulfur and preferably from 3 to 15% by weight, and at a maximum 5% nitrogen and preferably less than 1% by weight. Those which have a strong acid function such as hydrocracking catalysts, whose base is an amorphous or crystallized aluminum silica (zeolite) and containing in general nickel or cobalt and molybdenum or tungsten, aluminum and possibly silicon, phosphorus, fluorine, boron or any other suitable additive, must contain from 1 to 20% by weight of sulfur and from 0.05 to 10% by weight of nitrogen and preferably from 3 to 15% by weight of sulfur and from 0.1 to 3% by weight. The catalysts are charged into the unit which is then purged under nitrogen, then under hydrogen and then pressurized according to the usual procedures. The catalytic beds are then brought to a temperature less than 250°C and preferably less than 180°C. The liquid feed is then injected. The preferred temperature range for the injection is between 120 to 180°C. This liquid feed, different from the nominal feed of the unit, is a petroleum cut of the kerosene or gas oil type, preferably coming from the atmospheric distillation column, with a bromine index less than 5 and preferably less than 2, with a final distillation point below 450°C and preferably below 400°C, with a sulfur content greater than 0.1% by weight and preferably greater than 0.3% by weight and with a nitrogen content less than 0.5% by weight and preferably less than 0.2% by weight. Additions of sulfur and nitrogen to this feed are not necessary, because the catalyst already contains enough. The operating conditions, in terms of the flow rates of liquid and gas, are the same as just described for the first activation procedure.

The catalyst temperature is increased while the liquid appears at the level of the high pressure separator at the rate of a slope between 1 and 100°C/hour and preferably from 5 to 50°C/hour up to a final stage between 310 and 370°C, the duration of which is several hours. The temperature increase can also be discontinuous, moving through different temperature stages. At the end of this stage, the catalyst is then activated and the feed of the unit can then be injected, preferably in a progressive manner. It should be noted that during the activation phase, the liquid feed is preferably recycled, after passing through the reactors, up to the charging box, in order on the one hand to economize on gas oil, and on the other hand because slight loss of sulfur occurs by

dissolution and it may therefore be preferable to recover this sulfur for the purpose of sulfurization by recycling it on the catalysts.

It should also be noted that there is an exothermic reaction during this activation phase due to conversion of sulfuric oxides. This phenomenon can generally be observed at a temperature between 50 and 200°C. The corresponding temperature increase is greater if the liquid feed has not yet been injected, removal of calories being less efficacious in the dry phase than in the liquid phase.

These two procedures as described previously can also be used together. Thus you could use external injection of sulfurized and nitrogenated compounds, using an already presulfurized, already passivated catalyst. You could also just presulfurize the catalysts before charging the unit and use an injection of nitrogenated compound during the activation phase of the catalysts.

When the unit has several reactors in series or in parallel, which is frequently the case for hydrocracking units, the procedures for activation of different or identical catalysts in each reactor, and in particular temperature increases, may be simultaneous and identical in each reactor, or staggered over time. In the case where the unit has two reactors, and if the operation of the unit so permits, the second reactor can be activated first, at least in part, then the first reactor can be activated, and finally the activation of all the catalytic beds can be terminated.

The examples below illustrate this invention in a non-restrictive manner:

Example 1.

Two catalysts from the PROCATALYSE company are used: one is HR 348 comprised of 2.7% nickel oxide, 16.5% molybdenum oxide, with an aluminum base; the other, HYC 642, comprised of 2.6% nickel oxide, 12.7% molybdenum oxide, also contain a type Y zeolite.

These catalysts are charged into a catalytic test unit comprising two reactors, at the rate of 50 ml of HR 348 in the first reactor and 50 ml of HYC 642 in the second reactor. The charging densities of the 2 catalysts are respectively 0.88 and 0.82.

The feed used to conduct the hydrocracking tests is a distillate under vacuum, the analysis of which is shown in Table 1:

Table 1

| | |
|--|-------|
| Density (d^{15}_4) | 0.905 |
| Viscosity at 100°C (cSt or mm ² /s) | 5.4 |
| Sulfur (% by weight) | 1.6 |
| Nitrogen (% by weight) | 0.065 |
| Distillation (°C) (initial point) | 345 |
| ASTM D 2887 (50% point) | 425 |
| (final point) | 562 |

The feed used to carry out the liquid-phase activation is an atmospheric gas oil, the analysis of which is shown in Table 2:

Table 2

| | |
|-----------------------------------|-------|
| Density (d^{15}_4) | 0.839 |
| Sulfur (% by weight) | 0.40 |
| Nitrogen (% by weight) | 0.015 |
| Bromine index | < 1 |
| Distillation (°C) (initial point) | 150 |
| ASTM D 2887 (50% point) | 288 |
| (final point) | 395 |

The operating procedure used for tests of catalytic activity is described below. The catalysts are loaded into the unit. The pressure is adjusted to 13 MPa and the hydrogen flow rate to 28 liters TPN/hour. The activation method, as described in the examples below, is applied. When at the end of the activation procedure, the temperature is 150°C, the hydrogen flow rate is brought to 85 liters TPN/hour. The distillate feed under vacuum is then added at a flow rate of 85 ml/hour, and the temperature of catalysts HR 348 and HYC 642 is then brought to 385°C and 360°C respectively at a rate of 40°C/hour starting with the first catalyst and staggering the two temperature evolution curves from one another by 2 hours. After regular operation for 72 hours, the performance is measured in terms of net conversion. The latter is expressed by amount of products formed in the hydrocracking conversion, the boiling point of which is less than 360°C. The exact definition of the conversion,

expressed in %, is the following, with a_i and a_f being the weighted proportion of products with boiling point above 360°C in the initial feed and in the final effluent, respectively:

$$C = \frac{a_i - a_f}{a_i} \times 100$$

For the feed used, the value of a_i is 0.95. The catalytic performances corresponding to the different activation methods are given in Example 9.

Example 2

This example, which is not in accordance with the invention, described an activation procedure using H_2 , H_2S and NH_3 gases. The catalysts HR 348 and HYC 642 are loaded into the unit as described in example 1, and under pure hydrogen are brought to a temperature of 150°C. The hydrogen is replaced in favor of a H_2/H_2S mixture with a composition of 97/3 by volume, at a flow rate of 85 liters/hour. After a stabilization period of 2 hours, the temperature is brought to 340°C at the rate of 30°C/hour, then held for 2 hours at 330°C, and finally lowered to 150°C in about 3 hours. The H_2/H_2S gas mixture is replaced with hydrogen and the procedure is recommended as described in example 1.

Example 3.

This example is not in accordance with the invention. It consists in gas-phase activation of a catalyst presulfurized by an organic polysulfide and passivated by a nitrogenated compound. To presulfurize the HR 348 catalyst, a solution of organic polysulfide is prepared as follows. 5 parts per volume of TPS, a product manufactured by ELF AQUITAINE and containing 37% by weight sulfur, are added to 5 parts per volume of white spirit. The HR 348 is dry-impregnated by this solution in such a way that the added sulfur content will be 7.5% by weight, and the solvent is evacuated by heating under nitrogen to 150°C, then under reduced pressure of 10 mm of mercury, or 1333 Pa. The HYC 642 is impregnated in the same manner except that the solution is composed of

50% by weight of white spirit, 47.5% by weight of TPS 37 and 2.5% by weight of aniline. Sulfur and nitrogen contents are respectively 7.7 and 0.2% by weight. The two catalysts treated in this manner are charged into the test unit at the rate of 50 ml per reactor. The unit is heated under hydrogen up to 150°C, held for 2 hours at this temperature, then heated up to 330°C at a rate of 30°C/hour, then quickly brought back down to 150°C. The activation procedure is then terminated, and the test protocol is recommenced as described in example 1.

Example 4.

This example is not according to the invention. It describes a liquid-phase sulfurization procedure which does not include passivation of the catalyst's acid sites. The fresh catalysts in the oxide state are loaded into the unit, then heated to 150°C under hydrogen. Then atmospheric gas oil, composed as described in Table 2, and which has had 2% by weight of dimethyl disulfide added to it, is injected. The temperature is left at 150°C for 2 hours, then brought to 330°C at a rate of 30°C/hour, then left at 330°C for 2 hours, then brought back down for about 3 hours at 150°C. During the 330°C activation phase, a temperature stabilization problem was encountered, indicative of the presence of a strongly exothermic reaction. In addition, no liquid collected in the receiving vessel, because the gas oil was completely converted into light gas. This procedure is therefore not acceptable because its extrapolation to the industrial scale would be dangerous due to the strong exothermic nature of the cracking reaction which takes place on the non-passivated sites of the zeolite. We did, however, continue the procedure, lowering the temperature to 150°C and injecting into it the distillate under vacuum, as for the other examples.

Example 5

This example is according to the invention and describes a procedure for activation of a catalyst charged in the oxide state by a gas oil with sulfurized and nitrogenated compounds added.

The catalysts are charged, then heated to 150°C under hydrogen and the atmospheric gas oil (Table 2), with 2% by weight of dimethyl disulfide and 0.5% by weight aniline added, is injected at this temperature. The procedure is then continued as in example 4. At 330°C, the gas oil is still not

cracked and 98% of the liquid is recovered (the sulfur of the gas oil and of the dimethyl disulfide is converted into hydrogen sulfide). After the stage at 330°C for 2 hours, the temperature is lowered to 150°C, then the distillate under vacuum is injected as in the other examples.

Example 6

This example is according to the invention and recommences the conditions of the preceding example but replacing the sulfurized and nitrogenated compounds with dimethyl sulfide and n-butylamine. The sulfur and nitrogen contents in the gas oil are 1.4% and 0.1% by weight respectively, which corresponds to the conditions in example 5.

Example 7

This example is not according to the invention and describes a procedure for liquid-phase activation of presulfurized but not passivated catalysts. The HR 348 and HYC 642 catalysts are impregnated with a 50/50 solution of white spirit and with TPS 37 then processed at 150°C as done in example 3. The sulfur content is 7.5% by weight for HR 348 and 7.8% by weight for HYC 642. These two catalysts are charged, then heated to 150°C. The atmospheric gas oil, analyses of which are shown in Table 2, is then added and the temperature brought to 330°C. As described in example 4, a problem with temperature stabilization was observed and there was no liquid at the output of the unit due to a strong cracking reaction. After 2 hours of stage, the temperature was lowered to 150°C and the distillate under vacuum added.

Example 8

This example, which is according to the invention, describes a procedure for liquid-phase activation of presulfurized catalysts which have been passivated using a nitrogenated compound. The conditioning procedure performed on catalysts before charging into the unit follows the one described in example 3. The HR 348 contains 7.5% by weight of sulfur and HYC 642 contains 7.7% by weight of sulfur and 0.2% by weight of nitrogen. The catalysts are charged into the unit, heated to 150°C under hydrogen. The atmospheric gas oil, without a nitrogenated or sulfurized

compound added, is injected. After 2 hours of stabilization, the temperature is brought to 330°C at the rate of 30°C/hour, held for 2 hours and brought back down to 150°C. The distillate under vacuum is then injected. No cracking of the gas oil was observed during the stage at 330°C, as in the case of example 5.

Example 9

Table 3 summarizes the conditions described in the different examples and the catalytic results measured after net conversion of the gas oil into products with a boiling point below 360°C. It appears that the procedures in examples 4 and 7 yield a poor performance, doubtless due to the fact that cracking of the gas oil on a catalyst being sulfurized causes premature coking of the catalyst. Moreover, the procedure would not be workable on an industrial scale. The best performances are obtained in the procedures using the gas oil, whether the sulfur and nitrogen are added in the form of additives or gas oil, or whether they are already present in the catalyst before charging into the unit. The gas-phase procedures yield results considerably inferior to the liquid-phase procedures.

Table 3

| Example | [conditioning] | | Activation | | | | Conversion (% by weight) |
|---------|----------------|---------|----------------|---------|------------------|-----------------|-----------------------------|
| 2 | - | - | H ₂ | - | H ₂ S | NH ₃ | 60 |
| 3 | Poly S* | Aniline | H ₂ | - | - | - | 62 |
| 4 | - | - | H ₂ | gas oil | DMDS* | - | 25 |
| 5 | - | - | H ₂ | gas oil | DMDS | Aniline | 76 |
| 6 | - | - | H ₂ | gas oil | DMS* | NBA* | 71 |
| 7 | Poly S | - | H ₂ | gas oil | - | - | 29 |
| 8 | Poly S | Aniline | H ₂ | gas oil | - | - | 78 |

* Poly S : organic polysulfide (TPS 37)

DMDS : dimethyl disulfide

DMS : dimethyl sulfide

NBA : n-butyl amine

CLAIMS

1. Process for activation by at least sulfur or a sulfurized compound of a hydrocracking catalyst of a feed based on a petroleum cut, carried out before treatment of the feed (nominal feed) by injection of a liquid feed different from the nominal feed on the catalyst.
2. Process as claimed in claim 1 wherein said liquid feed is a light petroleum cut is a kerosene (or jet fuel) or a gas oil (or diesel).
3. Process as claimed in either of claims 1 or 2, wherein said light petroleum cut comes from the atmospheric distillation column.
4. Process as claimed in any of claims 1 through 3 wherein activation by sulfur is carried out in situ, that is, in the hydrocracking zone between 0.3 and 30 Mpa, under a hydrogen atmosphere, by injection at a temperature below 250°C of a liquid feed different from the nominal feed to be treated, with additional injection of a nitrogenated compound at a temperature below 270°C.
5. Process as claimed in claim 4 wherein the temperature of said injection is between 120 and 180°C.
6. Process as claimed in either of claims 4 or 5 wherein said liquid feed (light cut) is relatively free of diolefins and olefins and has a bromine index less than 5.
7. Process as claimed in claim 6 wherein the sulfur needed for the activation comes either from said liquid feed which therefore has a sulfur content between 0.1 and 3% by weight, or a sulfurized compound added at the time of said activation process.
8. Process as claimed in claim 7 wherein said sulfurized compound is chosen from among the group which comprises carbon sulfide, sulfides such as dimethyl sulfide, colloidal sulfur, disulfides such as dimethyl disulfide, thiophenic compounds, mercaptans, organic polysulfides,

the compounds containing sulfur associated with other functions and the sulfurized compounds capable of converting to hydrogen sulfide under the operating conditions of said activation.

9. Process as claimed in any of claims 4 through 7, wherein said nitrogenated compound is chosen from among the group comprised of primary, secondary and tertiary amines, compounds containing a quaternary ammonium, aryl amines such as members of the aniline family, pyrroles and their homologues, pyridines, nitriles, ureas and thioureas, nitrogenated, nitrous or nitrose derivatives, or any other basic compound or one capable of being converted into a basic compound.
10. Process as claimed in any of claims 4 through 7 wherein, during said injection of liquid feed and nitrogen, the temperature is progressively or discontinuously increased up to a temperature between 280 and 400°C, after which injection the (nominal) feed of the unit is added.
11. Process as claimed in any of claims 1 through 3 wherein:
 - (a) the catalyst, before entering the hydrocracking zone, has received (ex situ) quantities of sulfur and nitrogen sufficient to sulfurize the oxides and passivate the acid sites and
 - (b) the catalyst is charged in the hydrocracking zone which is purged under nitrogen, then placed under a hydrogen atmosphere, brought to a temperature below 250°C,
 - (c) a liquid feed different from the (nominal) feed having a sulfur content above 0.1% by weight and a nitrogen content below 0.5% by weight is then injected to trigger activation of the catalyst.
12. Process as claimed in claim 11 wherein said liquid feed is injected between 120 and 180°C.
13. Process as claimed in claim 11 wherein said liquid feed has a sulfur content above 0.3% by weight.
14. Process as claimed in claim 11 wherein said liquid feed has a nitrogen content below 0.5% by weight.

15. Process as claimed in any of claims 11 through 14 wherein it is carried out without additional addition of sulfur and nitrogen to said liquid feed, (outside of the sulfur and nitrogen it already contains).
16. Process as claimed in any of claims 11 through 15, wherein after the catalyst activation procedure carried out with progressive or discontinuous temperature increase up to a value between 310 and 370°C, the (nominal) feed of the unit is then added.
17. Process as claimed in any of claims 11 through 16 wherein said liquid feed is a petroleum cut of the kerosene or gas oil type.
18. Process as claimed in claim 17 wherein said liquid feed comes from the atmospheric distillation column.
19. Process as claimed in any of claims 1 through 18 wherein the catalyst, which has at least in part been presulfurized ex situ, is then activated in situ.
20. Process as claimed in any of claims 1 through 19 wherein a catalyst sulfurized and nitrogenated ex situ is then activated in situ.
21. Process for hydrocracking in several reactors, in series or in parallel, the different or identical catalysts in each of these reactors being activated together or at different periods as claimed in any of claims 1 through 20.